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Aliphatic and Polycyclic Aromatic Hydrocarbons concentrations in Sediment of Santos Estuary System

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ABSTRACT

This study present and discusses the results of the analysis of aliphatic and polycyclic aromatic hydrocarbons in surface sediments from Santos Estuary System to evaluate the contamination status and distribution and identify possible potential risk for the biota using Sediment Quality Guideline (SQGs). During the winter/2010, surface estuarine sediment samples were collect from 16 sites distributed along the estuarine system including mangrove areas under urban, industrial and harbor influence zones. Aliphatic hydrocarbons were determined on a gas chromatograph equipped with flame ionization detector (GC-FID) and Polycyclic Aromatic Hydrocarbons were quantitatively analysed by a gas chromatograph coupled to a mass spectrometer (GC-MS). Total AHs and PAHs concentrations in the SES varied from 41 - 370 μg g^{-1} and 214.34 to 41758.56 ng.g^{-1}. The highest levels of AHs and PAHs were found at site affected by industrial and harbor activities. To estimate the potential adverse biological effects the PAHs data were compared with Canadian Legislation, which set limits for PAHs in marine e estuarine sediments: TEL (threshold effect level) and PEL (probably effect level). Sites 4, 5, 10, 11, 12, 13 and 14 presented concentrations of individual and/or total PAHs above the TEL and PEL limits. Therefore, based on SQG approaches, adverse biological effects might be observed mainly in sediments surrounding the Cubatão industrial complex and harbor system.

1. INTRODUCTION

The Santos Estuary System (SES), located on the southeastern Brazilian coast lies in one of the most economically important areas of Brazil, composed of 23 large factories including a steel mill, an oil refinery, fertilizer, cement and chemical/petrochemical plants (the Cubatão industrial complex) that sum up to 260 pollutant emission sources. The largest commercial harbor of South America (Santos harbor) is also located inside the estuarine system, which is densely urbanized [1].

The SES (fig 1) has been characterized by increasingly intensive anthropogenic activity over the last 100 years, where the combustion of fossil-fuels in industrial and human activities contribute to the input of a large amount of particulate material rich in pollutants such as hydrocarbons. The increase in the intensity of urbanization and industrialization on the banks of the estuary, mainly over the last 50 years, has been responsible for the degradation of the mangrove vegetation, the emission of industrial effluents and the discharge of domestic sewage and solid residues [2]. In additional, port activities involve oil, sand and other transportation and fishing activities. The tourism is the second economic activity and attracts many people for the region. Apart from outstanding economic importance SES has also

considerable environmental relevance since the estuary is surrounded by mangrove swamps, which account for 43% of the total mangrove area of the state of São Paulo [3].
Sediments are an important environmental compartment for aquatic evaluations, since they may accumulate contaminants in concentrations higher than those observed in the water column, producing negative effects to the benthic biota and to the organisms that feed on the benthos or on the sediment. As a consequence of the low hydrodynamic of the estuary, high percentage of fines and the intense industrial activities, organic pollutants such as aliphatic hydrocarbons (AH) and polycyclic aromatic hydrocarbons (PAHs) are present in the sediments of SES [2, 4-6]. Besides, it must be taken in consideration that the SES commercial and subsistence fishing activities (mussels, crabs and fish) have been realized and the estuary is largely used to recreation, several inhabitants are living in constant primary contact with the water and sediments in suspension. Resuspension of sediment or bioturbation of sediment into the water column are believed to play a significant role in bioaccumulation of these compounds in the food web.
Aliphatic hydrocarbons are an important lipid fraction present in the estuarine sediments. Their sources are either natural, from photosynthesis by marine biota inhabiting the surface waters, or anthropogenic, from land run-off, fallout, and/or industrial input [7]. In sediments contaminated by oil, the aliphatic fraction is composed of a wide spectrum of n-alkanes, branched compounds and also of an unresolved complex mixture (UCM) that consists, primarily, of a multitude of branched and cyclic compounds with very similar physical properties and largely unknown structures (up to 250,000 substances) that cannot be resolved by capillary columns [8, 9]. This feature is normally associated with degraded or weathered petroleum residues [10].
Polycyclic aromatic hydrocarbons (PAHs) are compounds prevalent in the sediments of modern estuaries. PAHs are mainly derived from anthropogenic sources including the combustion of fossil-fuels, the long-range atmospheric transport of PAHs adsorbed onto soot or particulate matter, urban run-off derived from the abrasion of street asphalt and automobile tires, vehicular emissions and spillages of petroleum and by-products which contain complex assemblages of PAHs [11, 12].
This study present and discusses the results of the analysis of aliphatic and polycyclic aromatic hydrocarbons in surface sediments from Santos Estuary System to evaluate the contamination status, distribution, pollution sources and identify possible potential risk for the biota using Sediment Quality Guideline (SQGs).

2. MATERIAL AND METHODS

2.1 Sampling

Sixteen surface samples sediment (top 5 cm) were collected in 2010 in the SES, at the sites shown in Fig. 1, with a sediment grab sampler in order to evaluate hydrocarbon inputs from natural and anthropogenic sources. Some sites were chosen close to the main oil company in Brazil (sites 10, 11 and 12) and the local steel industry (sites 13, 14 and 15) which according to many studies, release emission with metals from their current industrial processes. Control sample was collected at Casqueiro river (site 16). This choice was supported by the fact that Casqueiro river is a sheltered region, geographically far from activities of Baixada Santista metropolitan region. The samples were placed in precleaned aluminum boxes, and then stored in a freezer at 15^{o}C until laboratory analysis.

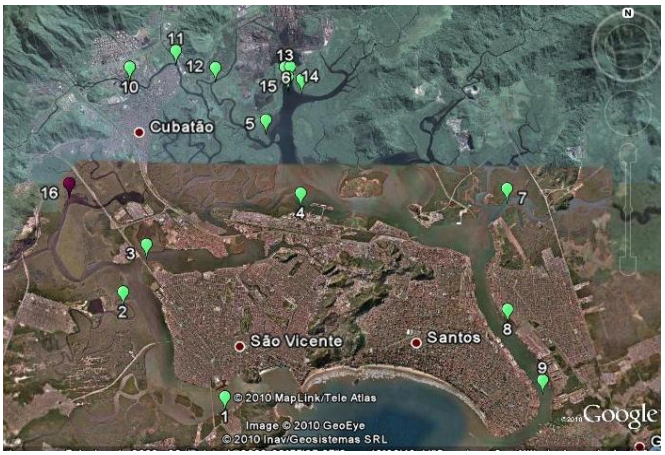

Fig 1: Santos Estuarine System and sites where sediments were sampled. (Source: Google Earth)

2.2 Extraction and fractionation

The sediment samples were lyophilized for 72 hours and an amount of 20 g was Soxhlet-extracted with a 50% mixture of residue grade n-hexane and dichloromethane for 8 h [13]. Before extraction, n-hexadecene, n-eicosene, d_8-naphthalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-chrysene and d_{12}-perylene were added to all samples, blanks and reference material (NIST – SRM 1944) as surrogates. The organic extracts were concentrated on a rotary evaporator and desulphurised with activated copper. The hydrocarbon extracts were fractionated into F1 (aliphatics) and F2 (aromatics) by silica gel–alumina chromatography column.

2.3 Instrumental analysis

Aliphatic hydrocarbons were determined on Agilent Technologies 6590 gas chromatograph equipped with flame ionization detector (GC-FID). PAHs were quantitatively analysed by an Agilent 6890 gas chromatograph coupled to a 5973N mass spectrometer (GC-MS) in the selected ion monitoring (SIM) mode. A 25x0.25 mm i.d.x0.25 µm HP 5MS film capillary column from Agilent was temperature programmed from 40^{o}C to 60^{o}C at 20^{o}C min^{-1}, 60^{o}C to 300^{o}C at 4^{o}C min^{-1} and held at 300^{o}C for 10 min in both GC-FID and GC–MS. All compounds were identified and quantified based on analytical curve built with by injection of certified standards at five different concentrations. PAH identification was based on GC retention times of certified standards, individual mass spectra and comparison with literature and library data. The detection limit (LD) of the method was 0.001-0.034µg.g^{-1} for n-alkanes and 1.00-3.70ng.g^{-1} for PAHs.

3. RESULTS AND DISCUSSION

3.1 Aliphatic Hydrocarbons

The total aliphatic hydrocarbons (AHs) in sediments include all resolved compounds of fraction 1, mainly n-alkanes and isoprenoids and the unresolved complex mixture (UCM).
Total AHs concentrations in the SES varied from 41 - 370 µg.g-1 and are presented in table 1. The highest levels of AHs were found at site 15 (370 $\mu g.g^{-1}$), located in the channel where loading and unloading operations are carried out by several factories of the Cubatão Industrial Complex. Sites 13 (357 $\mu g.g^{-1}$), 5 (188 $\mu g.g^{-1}$), 10 (187 $\mu g.g^{-1}$), 12 (110 $\mu g.g^{-1}$), 8 (109 $\mu g.g^{-1}$), 6 (109 $\mu g.g^{-1}$) and 14 (102 $\mu g.g^{-1}$) are also affected by industrial activities of Cubatão. According to Volkman et al., [8] and Readman et al., [10] levels of total AHs concentration below 10 $\mu g.g^{-1}$ are typical of unpolluted sediments but when significant inputs hydrocarbons occur concentrations may attain 100 $\mu g.g^{-1}$. Site 11 presented a relatively low concentration though it is near to the Cubatão industrial complex. A possible explanation might be the high percentage of sand that does not favor organic contaminants adsorption. The relatively high concentration at site 8 (109 $\mu g\ g^{-1}$) might be related to the proximity of a shipyard and very intense shipping traffic.

Table 1 Aliphatic hydrocarbon (µg g^{-1}dw) concentrations in sediment samples from the Santos Estuary System

Compounds/Site	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16
C12	0.034	0.008	0.018	0.015	0.035	0.023	0.016	0.055	0.261	0.017	0.031	0.043	0.326	0.077	0.235	<LD
C13	0.062	0.016	0.024	0.026	0.039	0.032	0.029	0.108	0.336	16.282	0.064	0.061	0.427	0.113	0.343	<LD
C14	0.049	0.016	0.018	0.019	0.035	0.027	0.028	0.083	0.231	0.016	0.052	0.058	0.381	0.078	0.25	<LD
C15	0.046	0.018	0.03	0.031	0.072	0.043	0.037	0.088	0.159	0.05	0.148	0.236	0.392	0.061	0.233	0.021
C16	0.026	0.015	0.017	0.021	0.038	0.026	0.016	0.046	0.088	0.026	0.068	0.054	0.307	0.034	0.137	<LD
C17	0.071	0.036	0.083	0.085	0.183	0.059	0.044	0.102	0.13	0.249	0.322	0.513	0.435	0.066	0.287	0.037
Pristane	0.049	0.019	0.026	0.048	0.056	0.027	0.015	0.053	0.142	0.146	0.451	0.366	0.238	0.037	0.173	<LD
C18	0.027	0.015	0.016	0.02	0.042	0.035	0.013	0.042	0.065	0.044	0.096	0.109	0.216	0.029	0.125	<LD
Phytane	0.035	0.026	0.021	0.033	0.044	0.031	0.014	0.052	0.092	0.121	0.324	0.296	0.119	0.025	0.128	<LD
C19	0.045	0.026	0.043	0.062	0.165	0.084	0.031	0.077	0.1	0.127	0.277	0.309	0.322	0.046	0.225	0.029
C20	0.031	0.021	0.028	0.032	0.04	0.058	0.023	0.042	0.075	0.021	0.024	0.054	0.193	0.035	0.112	0.024
C21	0.07	0.065	0.091	0.079	0.215	0.121	0.082	0.118	0.132	0.052	0.081	0.163	0.3	0.083	0.277	0.068
C22	0.055	0.044	0.067	0.051	0.163	0.086	0.057	0.105	0.148	0.082	0.151	0.186	0.275	0.07	0.207	0.051
C23	0.155	0.321	0.449	0.177	0.799	0.433	0.478	0.43	0.339	0.019	0.129	0.156	0.697	0.532	0.833	0.372
C24	0.134	0.243	0.372	0.263	1.156	0.625	0.259	0.222	0.366	0.049	0.194	0.52	0.827	0.378	0.878	0.98
C25	0.394	0.859	1.31	0.627	2.258	1.28	1.409	1.254	0.748	0.067	0.511	0.437	1.814	2	2.556	1.219
C26	0.106	0.156	0.224	0.116	0.376	0.279	0.148	0.209	0.214	0.04	0.157	0.197	0.523	0.259	0.453	0.264
C27	0.709	1.214	1.607	0.79	3.069	2.096	1.355	1.24	0.887	0.095	0.72	0.902	2.749	1.878	3.329	2.001
C28	0.213	0.321	0.411	0.209	0.718	0.6	0.227	0.313	0.297	<LD	0.223	0.444	0.865	0.281	0.878	0.5
C29	1.564	2.413	3.368	1.461	6.365	4.07	1.959	2.021	1.795	0.32	1.994	2.981	0.494	2.458	6.575	4.289
C30	0.233	0.348	0.489	0.287	0.848	0.496	0.185	0.38	0.383	0.327	0.74	0.775	1.084	0.277	0.978	0.594
C31	0.867	1.213	1.593	0.807	2.796	1.46	0.795	1.142	1.327	0.389	2.54	3.404	4.456	1.153	4.251	2.083
C32	0.114	0.163	0.221	0.112	0.324	0.18	0.079	0.188	0.222	0.074	0.335	0.527	0.619	0.089	0.57	0.285
C33	0.48	0.622	0.746	0.413	1.227	0.624	0.383	0.569	0.725	0.138	1.06	1.351	2.005	0.477	1.996	0.908
C34	0.037	0.053	0.084	0.037	0.098	0.082	0.053	0.088	0.055	0.039	0.069	0.207	0.179	0.186	0.149	0.068
C35	0.123	0.145	0.186	0.113	0.267	0.149	0.083	0.192	0.239	0.06	0.263	0.43	0.448	0.092	0.42	0.191
Totals Aliphatics	51.3	41	67.6	75.4	188	109	45	109	77	187	84	110	357	102	370	56.9
Resolved Aliphatics	9.78	11.77	16.73	11.64	41.75	23.39	12.6	16.28	18.69	15.97	36.42	47.46	54.88	17.48	50.59	19.71
Totals n-alkanes	5.644	8.353	11.496	5.853	21.326	12.971	7.787	9.113	9.321	18.581	10.248	14.116	20.333	10.752	26.295	13.984
UCM	41.5	29.2	50.9	63.8	146.2	85.8	31.9	92.5	58.6	171.5	47.5	62.3	302.6	84.4	319.8	37.2

The historical contamination of AHs in the sediments of SES showed lower values ranging 1.08 - 4.29 $\mu g.g^{-1}$ [4]. In 2002, Abessa [14] showed a little increase of total AHs concentrations varied from 0.28 to 14.30 $\mu g.g^{-1}$. Medeiros e Bicego, [5] measured AHs concentrations in the sediments and they reported an increase in levels of total AHs, ranging from 0.7 to 170.80 $\mu g.g^{-1}$. Couple years latter, Bicego et al., [6] found an accentuated increase of AHs concentration in the sediments of SES, showing highest values reported of AHs, ranging from 17.1 to 2508 $\mu g.g^{-1}$, at inner portion of estuary. The present results showed a decrease of the total AHs concentration in the sediments of SES.
The presence of UCM in aliphatic hydrocarbon chromatograms may be used as a diagnostic criterion for indicate the input of petroleum in the environment [10]. All the sites presented UCM whereas the highest values were found in site 15 (319.8 $\mu g.g^{-1}$), 13 (302.6 $\mu g.g^{-1}$) 10 (171.5 $\mu g.g^{-1}$) e 5(146.2 $\mu g.g^{-1}$), indicating the presence of degraded or weathered petroleum residues.

3.2 Polycyclic Aromatic Hydrocarbons

Individual and total concentrations of PAHs for this study are given in Table 3. The ∑PAH concentrations varied from <LD to 41758 $ng.g^{-1}$(dw – dry weight). The sediment can be considered contaminated when the values are above 500 $ng.g^{-1}$, while moderately contaminated sediment present concentrations between 250 and 500 $ng.g^{-1}$ [15]. Low concentrations (<500 $ng.g^{-1}$) occurred in sites 1, 2 and 16 which were collected far from major industrial and urban centers. High concentrations (>500 $ng.g^{-1}$) occurred at sites 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 which were collected near of the antropic sources. The site 15 presented values of recuperation under the limit accept for the method (60-120%), therefore the site 15 won´t be use for discussed the polycyclic aromatic hydrocarbons results.
The historical contamination of PAHs in the sediments of SES, have been reported by several authors. Nishigima et al., 4] showed concentration of the ∑PAH ranging from 80 to 42390 $ng.g^{-1}$ at inner portions of estuary. One year later, Abessa [14] reported concentration of the ∑PAH ranging from 1 to 42390 $ng.g^{-1}$ similar to Nishigima et al., [4] found in sediments of SES. In 2004, occurred a decrease of total PAHs in sediments measured by Medeiros e Bícego [5] showing levels ranging from 79.6 to 15389 $ng.g^{-1}$ in the sediment surrounding the Industrial Complex. Two years later, Bicego et al., [6] reported an increase of the ∑PAH in the sediment, whereas showed values ranging from 22.6 to 68130 $ng.g^{-1}$ in the same area. Cesar et al., [16] showed values of ∑PAH ranging from 106 to 950 $ng.g^{-1}$. The results present in this paper were similar to the concentrations found in the previous studies. However, the highest concentration of the ∑PAH was reported by Lamparelli et al., [3] in a systematic study along CETESB, in the sediments of SES, ranging from 11.62 to 733700 $ng.g^{-1}$ near the Cubatão industrial complex.
Different attention has been made for integrate available chemical and ecotoxicological data on environmental contaminants in order to establish Sediment Quality Guidelines (SQGs). The SQGs provide a basis to identify the concentrations of chemicals that can potentially cause adverse biological effects [17]. These proposed SQGs are intended as informal, non-regulatory effects-based benchmarks to support interpretation of complex chemical data [18]. Regulatory sediment quality criteria in Brazil, have not been established yet (Bicego et al., 2006). The Canadian Council of Ministers of the Environment (CCME) [19] uses the TEL/PEL approach, which is derived from geochemistry, toxicity and benthic community data and was adopted by Lamparelli, et al., [3].

Table 2 :Polycyclic aromatic hydrocarbons (PAHs) concentrations in sediment samples from the Santos Estuary System and TEL and PEL values (ng g-1 dw). Values above *TEL* are in bold and values above *PEL* are in bold and underlined.

Coumpouds/Sites	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P16	TEL	PEL
Naphthalene	2.61	6.58	18.94	**374.38**	**92.77**	16.83	11.7	8	16.82	**45.54**	**176.97**	**1548.35**	**150.08**	**783.59**	<LD	34.6	391
2-Ethyl-naphtalene	0.49	1.07	4.27	49.05	10.2	1.37	2.2	3.98	6.86	20.42	32.62	138.01	10.99	71.18	<LD		
∑- Metyl-naphtalene	2.23	5.02	13.6	237.7	53.3	7.63	8.9	11.36	35.89	95.71	203.46	739.4	60.35	358.09	<LD		
∑-Dimethyl-naphtalene	3.67	8.05	23.09	304.87	120.39	13.06	18.95	45.18	45.2	128.99	263.91	970.82	74.81	428.97	<LD		
∑-Trimethyl-naphtalene	3.48	8.31	27.97	122.96	93.41	14.36	17.68	34.47	16.22	85.07	121.67	521.55	50.2	258.67	<LD		
Biphenyl	1.01	2.32	4.96	151.01	27.35	4.83	4.37	5.56	3.67	30.28	67.39	421.49	33.97	160.85	<LD	5.9	128
Acenaphthilene	1.15	3.37	14.67	**454.24**	**167.08**	**32.2**	**20.08**	**12.46**	**13.47**	**64.59**	**94.47**	**495.66**	**77.44**	**210.65**	<LD	6.7	88.9
Acenaphthene	0.75	1.94	6.04	**75.27**	**34.02**	3.54	5.47	2.07	1.87	**12.18**	**33.46**	**829.71**	**78.8**	**409.16**	<LD		
Fluorene	1.14	2.96	7.73	**111.26**	**63.25**	10.06	6.82	6.46	10.19	**28.16**	**91.95**	**1042.2**	**105.03**	**399.62**	<LD	21.2	144
∑-Methyl-fluorene	1.44	6.99	10.02	94.76	60.42	45.09	16.19	16.27	8.36	83.25	85.86	388.42	52.85	196.12	<LD		
∑-Dimethyl-fluorene	1.8	3.25	10.33	36.69	23.85	6.64	8.27	7.49	21.23	184.98	47.56	312.9	28.43	168.61	<LD		
Dibenzothiophene	<LD	<LD	<LD	57.12	48.92	3.35	<LD	<LD	<LD	20.81	45.76	377.86	36.09	143.73	<LD	86.7	544
∑- Methyl-dibenzothiophene	0.97	1.57	4.87	31.18	10.37	3.13	2.89	1.7	1.22	10.21	11.89	152.35	14.39	84.89	<LD	46.9	245
∑-Dimethyl-dibenzothiophene	<LD	0.16	0.22	1.86	1.29	0.52	0.35	0.15	0.24	3.64	0.98	3.06	0.42	2.74	<LD		
Phenenthrene	4.52	11.77	29.49	**232.11**	**217.37**	53.2	31.64	13.06	38.27	**76.06**	**200.88**	**1746.51**	**203.18**	**968.37**	<LD		
∑-Metyl-phenanthrene	4.75	10.53	32.47	188.49	171.65	48.89	44.09	14.76	37.78	119.56	190.21	887.27	109.44	483.35	<LD		
∑-Dimethyl-phenanthrene	2.2	5.72	18.75	72.85	44.42	14.98	15.43	8.24	24.56	118.8	129.53	287.25	29.69	164.95	<LD		
Anthracene	1.47	3.11	11.15	**151.81**	**119.44**	14.35	10.94	4.3	17.34	23.8	**46.63**	**562.4**	**89.84**	**288.05**	<LD		
Fluoranthene	12.29	30.2	89.83	**683.78**	**915.6**	**221.46**	**136.98**	28.26	85.81	**251.06**	**273.17**	**2051.39**	**379.8**	**1883.82**	<LD	113	1494
∑-Metyl-fluoranthene	3.62	8.28	42.99	358.69	341.22	99.93	56.02	13.23	45.78	172.74	122.45	896.73	179.39	519.26	<LD	153	1398
Pyrene	12.58	29.94	88.48	**687.57**	**949.53**	**224.02**	137.89	28.42	87.01	**257.55**	**279.2**	**2154.63**	**397.93**	**1873.6**	<LD		
∑-Methyl-pyrene	3.79	7.77	35.58	170.82	140.29	46.34	42.58	8.3	118.93	327.73	253.55	422.23	65.14	317.48	<LD		
Benzo(a)anthracene	5.4	13.58	48.3	**445.61**	**461.77**	**151.37**	71.38	18.23	50.26	**89.7**	**138.68**	**1016.81**	**233.66**	**537.17**	<LD	74.8	693
Chrysene	6.99	17.94	65.26	**586.04**	**536.41**	**170.51**	85.44	21.08	92.37	**200.49**	**235.41**	**1728.96**	**319.27**	**1181.08**	<LD	108	846
∑-Methyl-chrysene	5.12	13.36	80.36	354.84	101.41	76.41	62.68	14.62	125.95	624.27	409.37	1229.16	120.75	828.16	<LD		
∑-Dimetil-chrysene	4.12	10.82	76.6	224.52	127.15	23.27	47.18	12.23	180.82	691.58	504.69	636.81	61.73	477.16	<LD		
Benzo(b)fluoranthene	14.91	27.07	108.07	888.81	575.72	176.61	178.76	40.36	83	169.94	179.5	1980.78	304.6	1140.88	<LD		
Benzo(j)fluoranthene	8.8	14.95	90.73	648.18	471.8	152.45	107.21	37.49	71.62	147.28	196.48	1985.72	280.17	1162.3	<LD		
Benzo(k)fluoranthene	8.19	16.92	75.98	643.2	534.13	202.04	113.91	22.42	51.33	148.29	164.94	1761.95	282.93	1412.25	<LD		
Benzo(e)pyrene	9.82	24.02	99.38	723.57	545.88	175.36	136.55	30.3	138.9	316.35	357.72	2005.54	323.5	1641.56	<LD		
Benzo(a)pyrene	9.65	24.56	**131.98**	**952.26**	**761.07**	**250.63**	**191.58**	31.11	**137.66**	**252.41**	**338.97**	**2519.24**	**461.43**	**1869.74**	<LD	88.8	763
Perylene	40.32	36.42	90.12	425.98	350.9	157.08	94.72	148.99	38.94	623.62	142.31	2697.92	319.6	736.18	<LD		
Indeno[123-cd]pyrene	13.54	32.87	148	959.75	831.38	290.9	234.59	122.45	77.72	151.03	219.45	2784.42	507.61	1249.74	<LD		
Dibenzo(ah)anthracene	2.71	**8.52**	**33.18**	**275.21**	**187.66**	**54.67**	**38.82**	**18.27**	**62.67**	**145.59**	**127.06**	**797.78**	**134.61**	**285.72**	<LD	6.22	135
Benzo(b)chrysene	1.73	4.29	26.16	174.34	130.63	46.14	35.77	14.96	39.46	100.94	99.85	580.62	100.04	161.05	<LD		
Benzo(ghi)perylene	14.14	32.6	131.65	935.46	701.24	233.59	194.34	105.28	116.7	231.92	319.79	2685.03	431.45	1311.75	<LD		
Coroneno	2.94	6.78	19.12	146.96	137.45	32.93	32.56	28.05	22.4	34.05	14.75	397.63	72.9	192.4	<LD		
∑PAHs	214.34	443.61	**1720.34**	**13033.2**	**10160.74**	**3079.74**	**2224.93**	939.56	**1926.52**	**6088.59**	**6222.54**	**41758.56**	**6182.51**	**24362.89**	<LD	1684	16770

TELs were calculated as the geometric mean of the 15th and 50th percentiles of the toxic effects and no effects data sets, respectively. PELs were derived by calculating the geometric mean of the 50th and 85th percentiles of the effects and no effects data sets, TELs were

intended as concentrations below which adverse effects on benthic organisms are expected rarely. In contrast, PELs were intended to represent concentrations above which adverse biological effects are expected frequently [6].
Sites 1 and 16 revealed no total and individual PAHs above the lower limits of the SQG, suggesting no adverse effects on the biota. Sites 2, 3 and 8 presented at least one of individual contaminants above of the TEL while sites 6, 7 and 9 presented seven, tree and four individual compounds above TEL respectively. Site 4 evidenced acenaftilene, benz(a)pireno and dibenz(a,h)anthracene above PEL limits. Site 5 presented concentrations of acenaphtilene and dibenz(a,h)antracene above PEL. Sites 10, 11 and 13 showed dibenz(a,h)anthracene concentrations above higher level of SQG. Sites 12 and 14 presented the highest concentrations of the total and individual PAHs above higher level of SQG. Such evidences as sites of concern 5, 10, 11, 12, 13 and 14 (located near the Cubatão industrial complex) regarding possible negative effects to the local aquatic biota.
The data presented in sites which extend from the central portion of the channels around Santos and São Vicente presented concentration above TEL for some individual PAH. According to Medeiros e Bícego, [5], this occurs probably influenced by the Cubatão industrial complex via atmospheric emissions. In general it was observed that the organic contaminants are probably deposited close to their source because of the limited water circulation, high percentage of fines and transport of particles in the SES [20].
According to the TEL/PEL criteria for PAHs, adverse biological effects might be observed in sedimentary deposits surrounding the Cubatão industrial complex principally in the Piaçaguera channel and in inner portions of estuary (sites 12 and 14) and in all sites except sites 1 and 16 that presented low concentrations of PAHs.

4. CONCLUSION

The historical contamination of the SES is well known and several times described in the literature. This study reveals a decrease of the total AHs concentration in the sediments. However, the total PAHs level presents an increase when compared with previous studies and the concentrations are above the SQG limits revealing an alarming levels of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, crysene, benzo(a)pyrene, dibenzo(ah)anthracene.
These high concentrations might result in bioaccumulations, carcinogenic and mutagenic effects on the aquatic biota and commercial seafood (i.e. crabs, oyster, fishes) and consequently risk for human health through diet habits.
Thus, is suggested the need a continuous monitoring be accomplished in the most contaminated areas of the SES that include toxicity tests and benthic community composition in order to match chemical data with the other two components of the sediment quality triad. For this reason, continuous studies have to be performed concerning the risk of public health in order to support policy makers towards and adequate mitigation initiatives focusing, mainly, to the low-income population living in the surroundings of the estuary , and are intrinsically in contact with these contaminated regions.

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